Growth and characterization of light emitting ZnS/GaN heterostructures

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Heterostructures involving ZnS/GaN show promise for the injection of holes from *p*-GaN into *n*-ZnS. Utilizing knowledge obtained from ZnS phosphor technology, this combination could result in a new type of multi-color electroluminescent display. Further, this combination provides a very interesting interface. Both ZnS and GaN are very ionic materials. Hence, it is desirable that the interface will be relatively benign, and that charge injection can occur despite the large lattice mismatch and resulting misfit defects that form near the interface. The highly lattice mismatched structures ZnS/GaN and ZnS/Al_2O_3 were grown by molecular beam epitaxy using elemental sources. Growth rates of up to 0.4 μm ph were observed for the lower growth temperatures, with rapidly diminishing rates for temperatures above 350 °C. The GaN substrate consisted of a 3 μm epilayer grown on sapphire (0001) by metalorganic chemical vapor deposition. Reflection high energy electron diffraction observations indicate that the zincblende ZnS layers commonly contain (111) twins, although films with no visible twin spots could be grown at a high substrate temperature. The sulfide layers were characterized using photoluminescence, x-ray diffraction, and scanning electron microscopy (SEM). X-ray peaks typically had widths of 400 arcsec for $\omega/2\theta$ scans, and somewhat worse for ω scans, indicating mosaic tilt. Photoluminescence spectra of the ZnS films doped with Ag and Al demonstrated the characteristic blue transition near 440 nm. SEM electron channeling patterns indicated that the ZnS films lie at a 30° rotated orientation to the Al_2O_3 (0001) substrate, as does GaN. *p*-GaN/*n*-ZnS devices were fabricated using standard photolithography techniques. The current voltage characteristics are reported and preliminary electroluminescence results are discussed for this heterojunction system. [S0734-211X(97)06804-2]

I. INTRODUCTION

Zinc sulfide, with its wide direct band gap, has long been known as a versatile and efficient light emitting compound. It has been extensively used as a phosphor, and continues to show promise in semiconductor light emitting devices, such as ZnS based flat panel displays,[1–3] light emitting diodes,[4] and semiconductor lasers.[5] However, difficulties in producing high quality doped material, particularly *p*-type, have otherwise reduced the utility of the sulfide system.

Recently, high conductivity *p*-type GaN has become available.[6–8] With a valence band edge below that of ZnS,[9] it has been proposed that GaN may be a good hole injector into ZnS and other light emitting semiconductor materials.[10] To this end, we have grown ZnS on GaN (0001) and sapphire (0001) substrates by molecular beam epitaxy (MBE) in an attempt to characterize this potentially interesting system as well as gain insight into highly lattice mismatched systems in general.

While there have been many reports of ZnS grown by MBE on near lattice matched substrates such as Si,[11,12] GaP,[13–15] and GaAs,[16–18] with lattice mismatches of 0.4%, 0.8%, and 4%, respectively, little has been reported of epitaxial growth on the highly mismatched substrates GaN ($\sim +20\%$ mismatch) or Al_2O_3 ($\sim -20\%$ mismatch). These interfaces are very interesting because of the large mismatch and the unusual properties of the constituents. First, it is not expected that the ZnS epilayer will grow coherently strained for more than 1 monolayer. More likely, relaxation in the layers closest to the interface will result in dangling bonds and numerous dislocations. In fact tilting and three dimensional (3D) relaxation are likely the most energetically preferred strain relaxation mechanisms.[19] Second, GaN and ZnS are known to be good light emitters even when the defect density is high. Hence, this interface provides us with a potentially technologically useful junction even though it is likely to be heavily defected.

II. MBE GROWTH AND RHEED OBSERVATIONS

ZnS epilayers were grown in a modified Perkin–Elmer 430 MBE system, equipped with a valved cracking source for sulfur (6 *N* purity), Knudsen cell sources for elemental Zn (6 *N*), Al (6 *N*), Ag (6 *N*), and a radio frequency nitrogen (5 *N*5)plasma source (Oxford Applied Research). Except where noted, the sulfur cracking zone temperature was held at 700 °C. The growth chamber maintains a base pressure during growth of 3×10^{-10} Torr with cryopaneling fully cooled. Samples were either bonded with In to molybdenum holder blocks, or secured to similar blocks with Mo or Si clips. We found that In bonding provided better temperature uniformity and reproducibility than the use of clips. Temperatures were measured by thermocouple, and reflection high energy electron diffraction (RHEED) operating at

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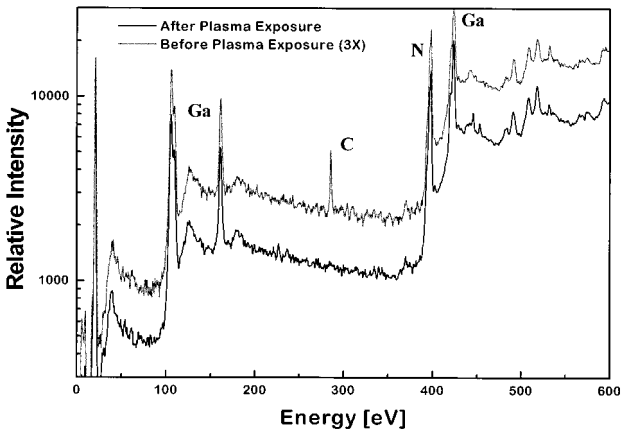

FIG. 1. X-ray photoemission spectrum of GaN before and after exposure to *in situ* rf nitrogen plasma.

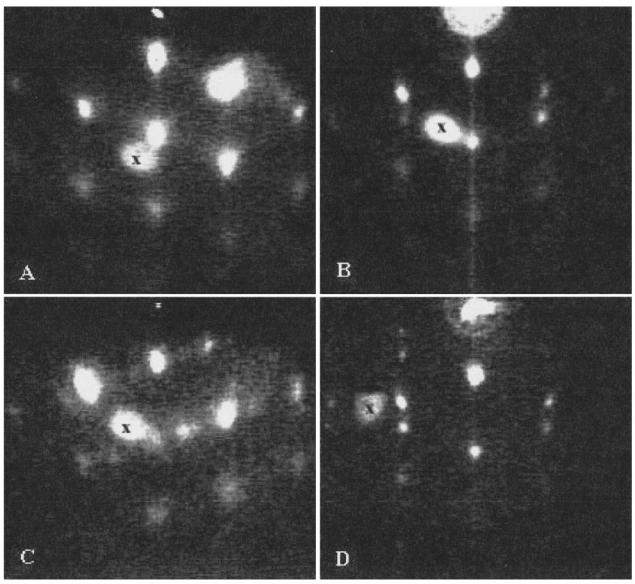

FIG. 2. 10 keV RHEED images [$(1\bar{1}0)$ azimuth] of ZnS on sapphire (A) grown at 400 °C with no visible twin spots, (B) grown at 250 °C with sulfur cracking zone temperature at 700 °C and showing (111) twins, (C) grown at 250 °C with cracking zone at 300 °C showing (111) twins, and (D) ZnS:Al,Ag grown on GaN [(111) twinned]. The smudge common to all pictures is due to a defect in the phosphor screen (x).

10 keV was used as a characterization tool during growth. Some ZnS films were doped with Ag and Al.

The GaN substrates consisted of a 3-μm-thick epilayer grown by metalorganic chemical vapor deposition (MOCVD) on *c*-plane sapphire. Van der Pauw Hall measurements performed on the GaN layers indicated *p*-type conductivity of 5 Ω cm, a carrier concentration of $\sim 2 \times 10^{17}$ cm^{-3}, and a mobility of 7 cm^2/(V s). Sapphire (0001) substrates were sourced from Union Carbide Crystal Products. Substrates were degreased in organic solvents and loaded into the MBE vacuum system. Before epilayer growth, the samples were transferred *in situ* between the growth chamber and an x-ray photoemission spectroscopy (XPS) analysis chamber. XPS analysis on the GaN layers revealed carbon surface contamination of atmospheric origin. It was found that the carbon could be removed by exposing the sample to a rf nitrogen soak at a substrate temperature of 500 °C for $\sim$20 min (Fig. 1). The plasma operated at a chamber pressure of 1×10^{-6} Torr and 200 W rf power. This treatment also visibly improved the RHEED pattern of the GaN. Contamination could be reduced, but not eliminated, by thermal cleaning alone. The sapphire substrates were thermally treated at 500 °C for 30 min prior to growth, after which sharp RHEED streaks were manifest. We found that etching of substrates made no noticeable difference.

Preceding MBE growth the GaN and sapphire substrates showed sharp RHEED streaks. After opening the source shutters the RHEED pattern quickly became spotty for most films, suggesting that growth proceeds in the 3D (Volmer–Weber) mode. The spotty pattern persisted throughout the growth period, and indicates that the ZnS films are of the zincblende structure with (111) orientation and are single crystalline or composed of mosaic crystallites which are aligned with the underlying substrate lattice. Most films displayed twinning in the (111) growth plane [Fig. 2(B)] which is commonly observed for growth on a (111) oriented substrate,[13,18] although this twinning was absent and replaced by (111) twins for some films grown with a lower sulfur cracking temperature of 300 °C [Fig. 2(C)]. Films grown at the higher temperature of 400 °C showed no visible twinning [Fig. 2(A)][20] and show superior surface morphology, although they suffer from extremely low growth rates. Antithetically, ringlike patterns were observed for films grown at very low temperatures or with poor surface preparation. Streaky patterns were not observed for any of the samples grown at temperatures between 150 °C and 400 °C and with source flux beam equivalent pressures (BEPs) of $(0.3-2.0)\times10^{-7}$ Torr.

III. FILM CHARACTERIZATION

Film thicknesses were measured by depth profiler and by spectroscopic ellipsometery, and growth rates were calculated assuming a constant rate throughout the growth period. Figure 3 shows the calculated rates as a function of growth temperature. Rates of up to 0.4 μm/h were observed for the lower growth temperatures, with rapidly diminishing rates for temperatures above 350 °C. This trend is in agreement with other work.[11,13,18] A typical film thickness was 600 nm.

Some films were characterized by scanning electron microscopy (SEM) operating in electron channeling pattern (ECP) mode. The ECP scans are useful as an indication of crystal symmetry, quality, and orientation. Channeling patterns were visible for as grown films grown at 400 °C and for post-annealed films. The ECP shown in Fig. 4 is of a sample annealed in sulfur over pressure at 1000 °C.[21] For films of poorer crystallinity as quantified by x-ray measurements, no ECP was visible. As confirmed by RHEED observations, the scan shows that the zincblende ZnS grows at a 30° rotated orientation to the sapphire substrate lattice. That is, the $(1\underline{1}1)$ faces of ZnS parallel the (0001) faces of Al_2O_3 and the [110]

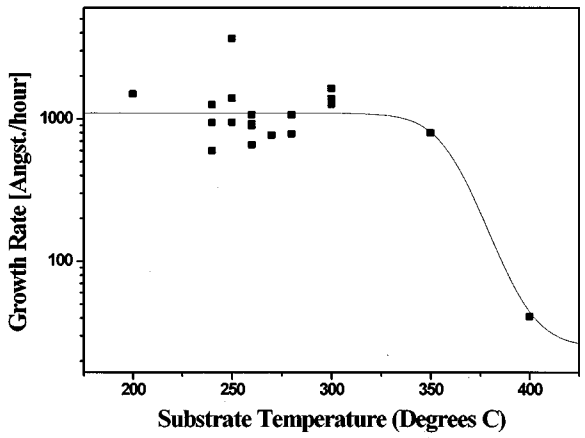

FIG. 3. Temperature dependence of the growth rate of ZnS on sapphire (0001). The line is meant to guide the eye.

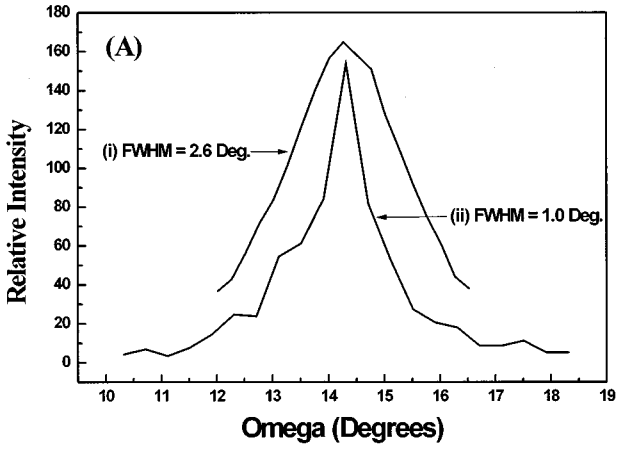

FIG. 5. X-ray rocking curves for ZnS grown on sapphire at (i) 250 °C and (ii) 400 °C.

azimuth points along the $[1\bar{0}10]$ direction (Miller–Bravais notation) of the Al_2O_3. GaN has also been observed to grow in a 30° oriented state on sapphire (0001). The degree of detail visible in the ECP also indicates good crystal quality.

High resolution x-ray diffraction analysis was performed using a four crystal [Ge (220)] diffractometer and Cu $K\alpha$ x rays. Results indicated that the films are composed of mosaic crystalline domains which are slightly tilted and rotated from one another. Such mosaic films are commonly observed in other materials systems where large lattice mismatch exists, such as Si on Al_2O_3, and GaAs on Si. The full width at half maximum (FWHM) of (111) peaks were consistently close to 400 arcsec for $\omega/2\theta$ scans, invariable with growth conditions. X-ray rocking curves (ω scans) showed peak widths of up to several degrees, depending on growth temperature, film thickness, and doping (Fig. 5). The FWHM of ω scans provides an indication of the degree of mosaic tilting that is present in the film. Undoped samples grown at 400 °C showed the best as grown rocking curve FWHM of ~60 arcmin. Further improvement in crystalline quality was obtained by post-annealing at 1000 °C in a high pressure sulfur environment.[21]

Low temperature (5 K) photoluminescence (PL) measurements were made using the 325 nm wavelength of a HeCd laser. The samples doped with Ag and Al produced a bright blue luminescence with spectra as shown in Fig. 6. Visible are the characteristic silver high (390 nm) and low (440 nm) energy emission bands.[22] The relative intensities of the two bands are known to be dependent on sample preparation. In the samples studied, both bands are present for the ZnS:Al,Ag films grown on sapphire, while the lower energy peak is dominant for the films grown on *n*-GaN, and the film grown on *p*-GaN shows only emission near the Ag higher energy wavelength. The *p*-GaN layer also has luminescence in the blue-violet region, and is not resolvable from the ZnS emission shown in Fig. 6(A). This variation in Ag transition peak intensities is not well understood at this time, and further study is warranted. Also present in Fig. 6(B) is the near band edge excitonic structure (350–400 nm) of the uninten-

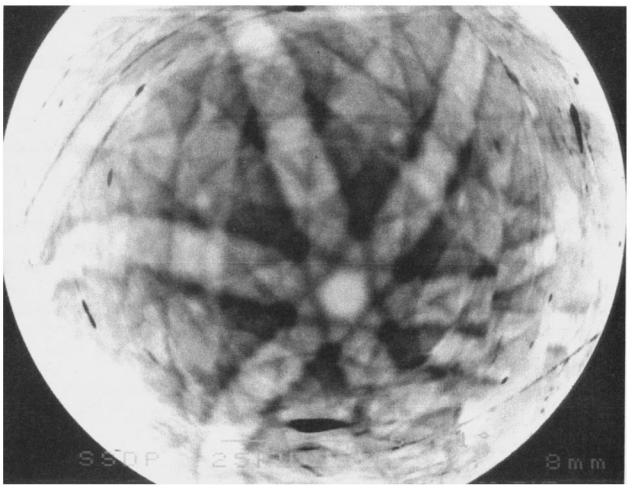

FIG. 4. Shown is the SEM electron channeling pattern of ZnS grown on sapphire (0001), post-annealed at 1000 °C under high sulfur over pressure. The ECP indicates that the ZnS layer lies rotated to the substrate. Distortion in the figure is caused by charging effects.

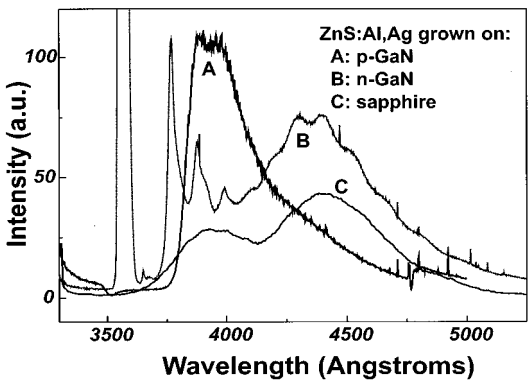

FIG. 6. Low temperature (5 K) photoluminescence spectra of ZnS doped with silver and aluminum on (A) *p*-GaN, (B) unintentionally doped *n*-GaN, and (C) sapphire (0001).

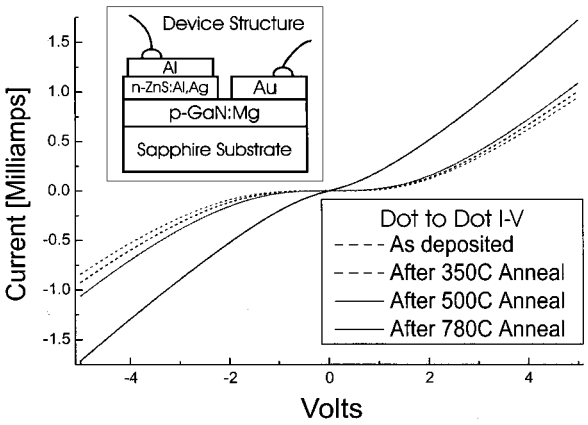

FIG. 7. Dot to dot current voltage characteristic of *p*-GaN as sputter deposited, and after subsequent anneals at 350 °C, 500 °C, and 780 °C for 1 min in nitrogen gas. The inset diagram shows the schematic structure of the fabricated *p*-GaN/*n*-ZnS device.

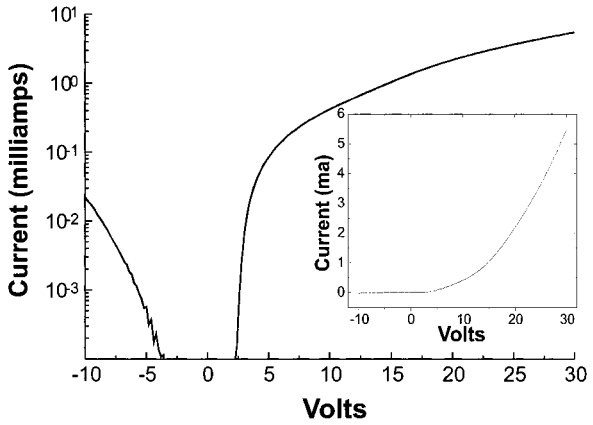

FIG. 8. Current-voltage trace of the prototype *p*-GaN/*n*-ZnS light-emitting device. Diode-like behavior is observed with large series resistance effects.

tionally doped *n*-type GaN substrate. The ZnS band gap is too wide to probe near band edge features with this laser.

IV. DEVICE FABRICATION

p-GaN/*n*-ZnS devices were fabricated using standard photolithographic processes. The insulating sapphire substrate necessitated the use of lateral contacts. The fully processed structure is shown in the inset of Fig. 7. An aluminum top contact was first sputter deposited on the as grown ZnS:Al,Ag/GaN:Mg layers. Mesas were then patterned and the Al and ZnS layers were etched in a solution of $Br:HBr:H_2O$ (1:100:100), which was found not to quickly etch the GaN. Au *p*-type contacts were then patterned and sputter deposited using a lift-off process. It is not believed that either contact is ohmic. The effects of annealing on the dot-to-dot current-voltage curves for *p*-GaN/Au contacts were observed on a separate substrate, and the results are presented in Fig. 7. As deposited, it is seen that the contacts are highly rectifying, and do not become fully ohmic even after annealing at 780 °C.

The current-voltage trace of the preliminary *p*-*n* device is shown in Fig. 8. It shows roughly diodelike behavior, although the nonideal effects of high series resistance and rectifying contacts are evident. Turn on voltage is seen to be ~3 V, which is expected, as it corresponds to the band gap of the materials. The necessity of lateral contacts and the low conductivity of GaN are largely responsible for the large series resistive component.

At low applied voltages (3–10 V), luminescence is observed by eye to be a pale blue similar to the hue observed in ZnS/*n*-GaN PL [Fig. 6(B)]. The devices are bright enough during room temperature operation to be seen with the room lights on with 1 mA current applied. The expected nonuniformity of luminescence due to current spreading is observed. Additionally, ''bright spots'' are seen which may be caused by defects or thickness variations in the ZnS layer. As forward bias is increased, light appears more violet colored, similar to low temperature ZnS/*p*-GaN PL [Fig. 6(A)]. The exact mechanism of luminescence is unclear at this time, as there are several possibilities. The rather broad photoluminescence spectra of the GaN:Mg and ZnS:Al,Ag samples were found to be quite similar at room temperature, thus making it difficult to deduce if recombination is taking place in the GaN layer or the ZnS layer. Other mechanisms, such as recombination in the nitride layer followed by absorption and fluorescence in the sulfide layer, are possible. Also, luminescence at high biases may be linked to hot carrier excitation processes. Due to the low temperatures of growth and device processing, we do not expect that a significant amount of interdiffusion has occurred, such as Zn diffusing into the nitride layer or Ga diffusing into the sulfide layer. Ga is known to act as a donor in ZnS, and Zn a deep acceptor in GaN. Spectroscopy and other work is in progress in the study of this structure.

V. SUMMARY

Zinc sulfide thin films were grown on GaN and sapphire substrates by MBE, with the GaN surface being effectively cleaned prior to growth by exposure to a rf nitrogen plasma. RHEED patterns indicated that monocrystalline films could be grown on both substrates, but most contained microtwins in the (111) or (111) planes. No twins were visible in the films grown at 400 °C. Typical growth rates were measured at 0.1–0.2 μm/h for temperatures below 350 °C and were much lower for higher temperatures. The samples were characterized using photoluminescence and x-ray diffraction. X-ray peaks typically had FWHM of 400 arcsec for $\omega/2\theta$ scans, and larger widths for ω scans, indicating a degree of mosaic tilts. The PL from the ZnS films doped with Ag and Al displayed bright blue luminescence. Heterostructure devices were fabricated and their current-voltage curves were measured. Electroluminescence from these devices was pale blue at low forward bias and shifted to violet at higher biases.

ACKNOWLEDGMENTS

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